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STERESELECTIVE OXIDATIVE ADDITION OF SILANES AND
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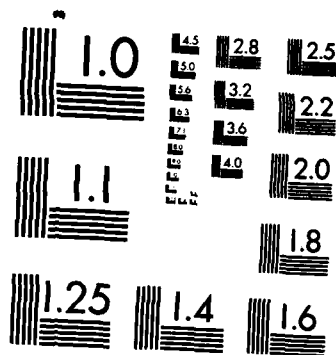
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Stereoselective Oxidative Addition of Silanes and Hydrogen Halides

to the Iridium(I) cis-Phosphine Complexes

$\text{IrX(CO)(1,2-bis(diphenylphosphino)ethane)}$, X = Br, CN

by

Curtis E. Johnson and Richard Eisenberg*

Prepared for Publication

in the

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Rochester, NY 14627

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The oxidative addition of silanes, $\text{R}_n\text{Cl}_3\text{-nSiH}$ ($n = 3, \text{R} = \text{Et}, \text{Ph}, \text{OEt}; n = 2, \text{R} = \text{Me}; n = 1, \text{R} = \text{Me}$), to the $\text{Ir}(\text{I})$ cis phosphine complexes $\text{IrX}(\text{CO})(\text{dppe})$ ($\text{X} = \text{Br}, \text{CN}$; $\text{dppe} = 1,2\text{-bis}(\text{diphenylphosphino})\text{ethane}$) has been found to proceed stereoselectively under kinetic control. Of the four possible diastereomers which can form by concerted cis addition of the Si-H bond to the iridium(I) center, the one having hydride trans to CO and Si trans to P(dppe) is formed initially with ~98% stereoselectivity. For $\text{X} = \text{Br}$, this diastereomer is not the thermodynamically favored product. Isomerization of the initially formed silyl hydride-			

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Product to the equilibrium mixture of diastereomers follows first order kinetics for the triphenylsilyl derivative with $k_1 = 0.015 \text{ min}^{-1}$. The rate of isomerization for the kinetic silyl hydride adducts decreases in the order $\text{Et}_3\text{SiH} > \text{Ph}_3\text{SiH} > \text{OEt}_3\text{SiH} > \text{Me}_2\text{ClSiH}$ with the Me_2ClSiH derivative not isomerizing even after prolonged heating. The most stable diastereomer for $\text{X} = \text{Br}$ has hydride trans to Br and silyl trans to P(dppe). For $\text{X} = \text{CN}$, the kinetic isomer with H trans to CO and Si trans to P(dppe) is also the most stable isomer, although other isomers are observed to form after initial reaction. Secondary chemistry of the triethylsilyl hydride products for $\text{X} = \text{Br}$ and CN is observed over longer reaction times leading to the formation of $\text{IrHX}(\text{CO})(\text{dppe})$ ($\text{X} = \text{Br}$), $\text{IrH}_2(\text{SiEt}_3)(\text{CO})(\text{dppe})$, and $\text{Et}_3\text{SiSiEt}_3$. This secondary chemistry is consistent with reductive elimination/oxidative addition sequences. The oxidative addition of HX to $\text{IrX}'(\text{CO})(\text{dppe})$ also proceeds stereoselectively, giving the isomer with H trans to X' and X trans to P(dppe). This diastereomer results from cis addition in which H-X approaches the square planar $\text{Ir}(\text{I})$ complex with its axis parallel to $\text{X}'\text{-Ir-P}$. Thus, while R_3SiH and HX both add to $\text{IrX}(\text{CO})(\text{dppe})$ by a cis concerted mechanism, the diastereoselection for HX is opposite to that for R_3SiH . It is proposed that this difference arises because the silane approach to the $\text{Ir}(\text{I})$ complex is nucleophilic while that of HX is electrophilic.

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Thermodynamic Oxidative Addition of Silanes and Hydrogen Halides
to the Iridium(I) cis-Phosphine Complexes

$\text{IrX}(\text{CO})(1,2\text{-bis}(\text{diphenylphosphino})\text{ethane})$, $\text{X} = \text{Br}, \text{CN}$

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Abstract: The oxidative addition of silanes, $\text{R}^n\text{Cl}_{3-n}\text{SiH}$ ($n = 3, \text{R} = \text{Et}, \text{Ph}$, OEt ; $n = 2, \text{R} = \text{Me}$; $n = 1, \text{R} = \text{Me}$), to the $\text{Ir}(\text{I})$ cis phosphine complexes $\text{IrX}(\text{CO})(\text{dppe})$ ($\text{X} = \text{Br}, \text{CN}$; $\text{dppe} = 1,2\text{-bis}(\text{diphenylphosphino})\text{ethane}$) has been found to proceed stereoselectively under kinetic control. Of the four possible diastereomers which can form by concerted cis addition of the Si-H bond to the iridium(I) center, the one having hydride trans to CO and Si trans to P(dppe) is formed initially with >98% stereoselectivity. For $\text{X} = \text{Br}$, this diastereomer is not the thermodynamically favored product. Isomerization of the initially formed silyl hydride product to the equilibrium mixture of diastereomers follows first order kinetics for the triphenylsilyl derivative with $k_1 = 0.015/\text{min}$. The rate of isomerization for the kinetic silyl hydride adducts decreases in the order $\text{Et}_3\text{SiH} > \text{Ph}_3\text{SiH} > (\text{OEt})_3\text{SiH} > \text{Me}_3\text{SiH}$ with the Me_3SiH derivative not isomerizing even after prolonged heating. The most stable diastereomer for $\text{X} = \text{Br}$ has hydride trans to Br and silyl trans to

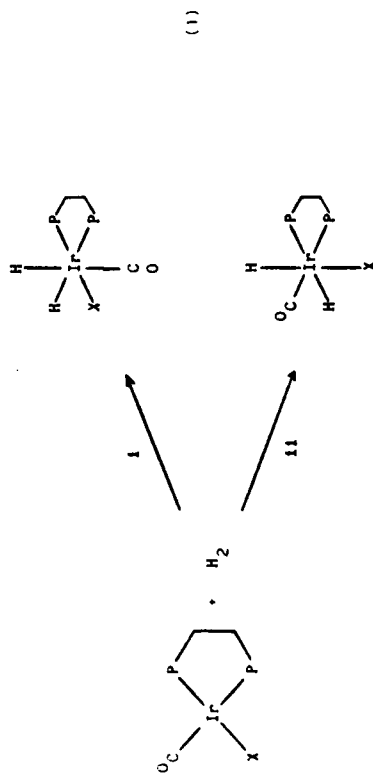
P(dppe). For $\text{X} = \text{CN}$, the kinetic isomer with H trans to CO and Si trans to P(dppe) is also the most stable isomer, although other isomers are observed to form after initial reaction. Secondary chemistry of the triethylsilyl hydride products for $\text{X} = \text{Br}$ and CN is observed over longer reaction times leading to the formation of $\text{IrHX}_2(\text{CO})(\text{dppe})$ ($\text{X} = \text{Br}$), $\text{IrH}_2(\text{SiEt}_3)(\text{CO})(\text{dppe})$, and $\text{Et}_3\text{SiSiEt}_3$. This secondary chemistry is consistent with reductive elimination/oxidative addition sequences. The oxidative addition of HX to $\text{IrX}(\text{CO})(\text{dppe})$ also proceeds stereoselectively, giving the isomer with H trans to X' and X trans to P(dppe). This diastereomer results from cis addition in which H-X approaches the square planar $\text{Ir}(\text{I})$ complex with its axis parallel to $\text{X}'\text{-Ir-P}$. Thus, while R_3SiH and HX both add to $\text{IrX}(\text{CO})(\text{dppe})$ by a cis concerted mechanism, the diastereoselection for HX is opposite to that for R_3SiH . It is proposed that this difference arises because the silane approach to the $\text{Ir}(\text{I})$ complex is nucleophilic while that of HX is electrophilic.

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Introduction

In previous reports we have described the kinetic stereoselectivity of H_2 oxidative addition to $IrX(CO)(dppe)$ complexes, ($dppe = 1,2$ -bis(diphenylphosphino)ethane), which are cis-phosphine analogs of Vaska's complex, $trans-IrCl(CO)(PPh_3)_2$.^{1,2} This oxidative addition can proceed along two possible pathways, I and II, as shown in eqn (1), leading to different diastereomers for the concerted cis addition of H_2 . Pathway I corresponds to



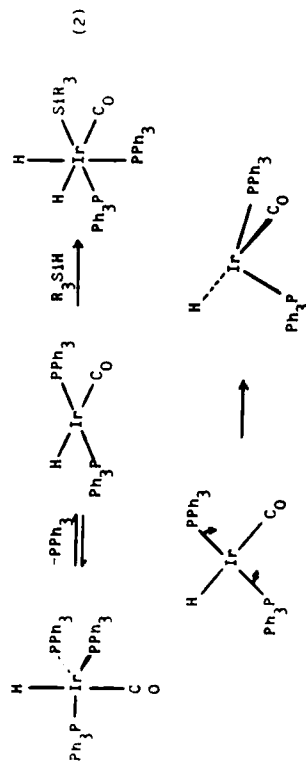
H_2 approach to the square planar complex with the molecular axis of H_2 parallel to $P-Ir-CO$ as shown in A. The concerted oxidative addition along I takes place with a bending of the $trans-P-Ir-CO$ axis so that one hydride of the product becomes $trans$ to CO and the other $trans$ to P . Pathway II corresponds to approach with the H_2 molecular axis parallel to $P-Ir-X$, as shown in B, and addition occurs with bending of the $P-Ir-X$ axis.



While two diastereomers for concerted H_2 oxidative addition to

$IrX(CO)(dppe)$ are thus possible, we have found that for $X = Cl, Br, I, H$, and CN , the initial oxidative addition takes place diastereoselectively along pathway I. The reaction proceeds under kinetic control as illustrated by the fact that for $X = Cl, Br$, and I , the diastereomer formed initially slowly equilibrates with the more stable diastereomer corresponding to oxidative addition along pathway II. Based on the variation of X , a steric basis for the diastereoselectivity of H_2 oxidative addition can be ruled out, leaving ligand electronic effects as the controlling factor in the diastereoselection process.

In order to probe more deeply the extent and basis of kinetically-controlled diastereoselectivity in oxidative additions, we have examined the reaction chemistry between $IrX(CO)(dppe)$ and the unsymmetrical substrates R_3SiH and HX . The oxidative addition of silanes to Iridium(I) complexes has been studied extensively.³⁻¹³ The reaction, which represents a required step in hydrosilation catalysis, is generally viewed as a concerted cis addition.¹⁴ However, this has only been demonstrated or established convincingly in a limited number of cases. In an elegant series of investigations, Harrod and coworkers have studied silane oxidative addition to $IrH(CO)(PPh_3)_3$ kinetically and stereochemically.^{3,4} Their analysis of the reaction in eqn (2) through the determination of activation parameters led them to the conclusion that silane oxidative addition and phosphine addition are mechanistically similar processes with activation enthalpies due mainly to deformation of the square planar complex prior to addition as shown in C.³



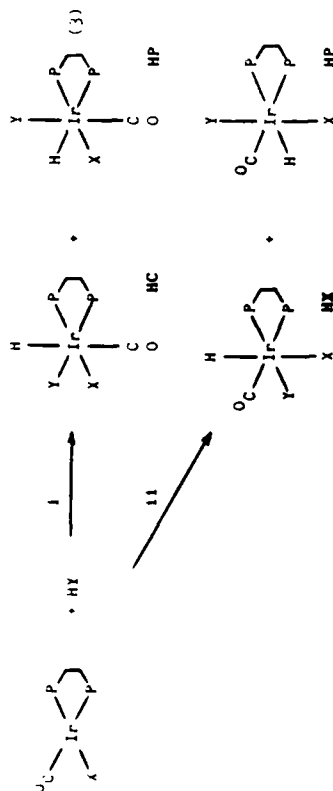
Through the use of deuterated silane substrate, Fawcett and Harrod showed that the hydride ligand trans to PPh_3 in the product of eqn (2) comes from the silane substrate in the cis addition process.¹⁴

In a different study, Bennett, *et al.*,⁷ examined silane addition to IrClL_3 ($\text{L} = \text{PPh}_3, \text{PMePh}_2, \text{AsPh}_3$) to give the Ir(III) allyl hydrides $\text{IrHCl(SiR}_3)_3\text{L}_n$ where $n = 2$ or 3 . In all cases, the silyl and hydride groups in the product complexes are mutually cis, and this result is taken as supporting, but not proving, cis concerted addition of silane. A definitive study of the stereochemistry of R_3SiH addition to Vaska's complex as it relates to the mechanism of the reaction has not been performed to date because of insufficient solubility of initial $\text{IrHCl(SiR}_3)_3(\text{CO})(\text{PPh}_3)_2$ products, and facile secondary reactions leading to dihydride products. However, a study by Sommer, *et al.*,¹⁰ using optically active silanes $\text{R}_3\text{Si}^*\text{H}$ showed that Vaska's complex promotes $\text{Si}^*\text{H/Si}^*\text{D}$ exchange with complete retention of configuration at Si, thereby giving support to the notion of cis concerted addition of silane to Vaska's complex.¹¹

The mechanism of HX addition to $\text{IrCl(CO)(PPh}_3)_2$ and its analogs has also been investigated.¹⁵⁻¹⁷ Vaska observed that gaseous HX oxidatively adds to $\text{trans-IrX(CO)(PPh}_3)_2$ ($\text{X} = \text{Cl, Br, I}$) in the solid state to form cis addition products.¹⁵ Blake and Kubota¹⁶ found that the cis stereochemistry of addition

also holds for the reaction in benzene or chloroform solution. In the presence of more polar solvents such as methanol, acetonitrile, water, or dimethylformamide, however, mixtures of cis and trans HX isomers are formed. Longato, *et al.*,¹⁷ established a similar stereochemistry of HX addition to crystalline $\text{trans-Ir(carb)(CO)(PPh}_3)_2$ (carb = $-2\text{-R-1,2-C}_2\text{B}_{10}\text{H}_{10}$ or the 1,7-carborane).¹⁷ The cis stereochemistry of addition to $\text{Ir(carb)(CO)(PPh}_3)_2$ is maintained in dry non-polar solvents, but mixtures of cis and trans addition products are found in wet benzene and $\text{CH}_3\text{OH-CH}_2\text{Cl}_2$ solutions, and only trans addition is seen for the complex containing the bulky ligand $-2\text{-CH}_3-1,2\text{-B}_{10}\text{C}_2\text{H}_{10}$. It thus appears that the stereochemistry and mechanism of HX oxidative addition to Ir(I) complexes of the type IrX(CO)L_2 depend on the reaction conditions and Ir(I) ligands, with cis addition occurring in non-polar media and the solid state.

For the cis-phosphine complexes IrX(CO)(dppe) used in the present study, cis oxidative addition of an unsymmetrical substrate HX corresponds to a double diastereoselection process in which the orientation of the HX substrate relative to the metal complex offers two possibilities for each of the pathways of addition shown in eqn (1). The four diastereomers for cis addition of HX to IrX(CO)(dppe) are shown in eqn (3). We will refer to the double diastereoselection process as diastereoselection (*ie.*, pathway 1 or 11) with specific substrate orientation. The relative orientation of HX in a cis concerted addition is given by the position of the hydride ligand in the product. For



oxidative addition along the P-Ir-CO axis, pathway I, two diastereomers are possible, the first with hydride trans to CO labelled as HC and the second with hydride trans to P labelled as HP. These two diastereomers correspond respectively to HY approach to IrX(CO)(dppe) shown as D and E. Similarly for

Pathway II (addition along the P-Ir-X axis), diastereomers with hydride trans to



X (HX) and hydride trans to P (HP) are possible, corresponding to substrate approaches shown as F and G. This manner of labeling the diastereomers of HY



addition by pathway of addition and ligand trans to hydride will be used throughout the rest of the paper.

Experimental Section

General. The following reagents were used as received: triethylsilane, triphenylsilane, triethoxysilane, chlorodimethylsilane, dichloromethylsilane, and tetra-*n*-butylammonium (TBA) bromide (Aldrich), HBr (Matheson, 99.8%), and ^{13}C (Monsanto Research Corp., 99%). Bis(triphenylphosphine)iminium (PPN) cyanide, $^{18}\text{IrBr}(\text{CO})(\text{dppe})^2$, and $^{19}\text{Ir}(\text{CO})(\text{dppe})^3$ were prepared by established procedures. Benzene- d_6 and acetone- d_6 (Aldrich Gold Label, 99.5% D) were distilled from Na/benzophenone and Linde 4A molecular sieves, respectively, for sealed-tube NMR experiments.

Reactions were generally carried out under a nitrogen atmosphere using a Schlenk-type vacuum line. Sealed-tube samples for ^1H NMR experiments were prepared on a high-vacuum line by condensing solvent and silane or HX reagent into a tube containing the Ir(I) complex.

^1H and ^{31}P NMR spectra were recorded on a Bruker WH-400 spectrometer at 400.13 and 162.00 MHz, respectively, and ^{13}C NMR spectra were recorded on a Nicolet QE-300 spectrometer at 75.48 MHz. Chemical shifts were generally calculated from residual solvent resonances (acetone- d_6 δ_{H} 2.04, benzene- d_6 δ_{H} 7.15, δ_{C} 128.0). IR spectra were recorded on a Perkin-Elmer 467 spectrophotometer. Elemental analyses were determined by Galbraith Laboratories, Inc., Knoxville, TN. Mass spectra were recorded on a Dupont 21-490 B mass spectrometer.

Reaction of $\text{IrBr}(\text{CO})(\text{dppe})$ with Et_3SiH . The reaction was carried out in a sealed NMR tube by first placing 7 mg of $\text{IrBr}(\text{CO})(\text{dppe})$ in a 5-mm tube attached to a 14/20 glass joint. On a high-vacuum line 0.5 mL of solvent (benzene or acetone) and the desired amount of Et_3SiH were condensed into the tube at -196°C , and the tube flame sealed. After thawing, the progress of the reaction was monitored by ^1H NMR spectroscopy. The isomerized product, $\text{IrHBr}(\text{SiEt}_3)_2$,

Results and Discussion

All of the oxidative addition reactions and subsequent chemistry described here were followed by ^1H NMR spectroscopy. The chemical shifts and splitting patterns of the hydride resonances provide in almost all cases unambiguous assignment of the stereochemistry of the oxidative addition products.

As noted above, concerted cis addition of H_2 to the Ir(I) complexes IrX(CO)(dppe) yields in principle four different stereoisomers. These arise from oxidative addition of H_2 to the square plane by either pathway I or II, each with either of two possible substrate orientations for the concerted process. For stereoisomers I-HC and II-HX, the hydride resonance shows cis coupling to two nonequivalent phosphines, and a chemical shift distinctive for the ligand trans to hydride. For stereoisomers I-HP and II-HP, the hydride resonance occurs in the range -7.7 to -8.6 ppm with a distinctive doublet of doublets pattern and large trans J_{PH} . The magnitude of this trans coupling, together with previously established reaction chemistry, provides the basis for distinguishing between stereoisomers I-HP and II-HP.

Reaction of Et_3SiH with IrBr(CO)(dppe) . A benzene sample of IrBr(CO)(dppe) and three equivalents of Et_3SiH yields a pale yellow solution after thawing and shaking for one minute, indicating nearly complete reaction of the orange-colored Ir(I) compound IrBr(CO)(dppe) . The ^1H NMR spectrum taken three minutes after thawing shows resonances assignable to two complexes of the type $\text{IrHBr(SiEt}_3\text{)(CO)(dppe)}$ along with peaks for unreacted Et_3SiH (NMR and IR data are collected in Table I). The hydride resonances appear as an approximate triplet at δ -8.48 containing two nearly equivalent cis phosphorus couplings (-17.8 Hz), and a doublet of doublets at δ -16.64 containing two cis phosphorus couplings (5.8 and 15.1 Hz). The relative amounts of the two hydride products are 38% (δ -8.48) and 62% (δ -16.64). Over the course of 20 minutes the hydride

complexed, was isolated as a white powder from benzene-pentane solution. Anal. Calcd for $\text{IrHBr}_2\text{OP}_2\text{Si}$: C, 48.64; H, 4.95; P, 7.60. Found: C, 48.71; H, 4.83; P, 7.80.

Reaction of IrBr(CO)(dppe) with Ph_3SiH , $(\text{EtO})_3\text{SiH}$, $\text{Me}_2\text{C(SiH)}_2$, and MeCl_2SiH . ^1H NMR studies of these reactions were carried out in nitrogen-purged septum capped NMR tubes using typically 3 mg of IrBr(CO)(dppe) and 1-2 equivalents of silane in C_6D_6 solvent.

Reaction of Ir(CN)(CO)(dppe) with Et_3SiH . The complex Ir(CN)(CO)(dppe) was prepared *in situ* by condensing 0.5 mL of acetone into an NMR tube containing 0.5 mmol of IrBr(CO)(dppe) and 6.7 mg (0.12 mmol) of PPN(CN)^+ . The mixture was shaken for one minute at room temperature to give a homogeneous orange solution. After cooling to -196°C , Et_3SiH was condensed in and the tube flame sealed.

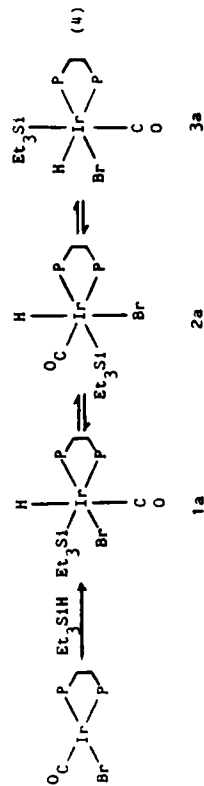
Reaction of IrBr(CO)(dppe) with HI . A C_6D_6 solution of IrBr(CO)(dppe) in a 5 mm NMR tube was purged with the gas evolved from the reaction of NaI with concentrated sulfuric acid using a nitrogen flow. This procedure, while not efficient for generating HI(g) , proved adequate for this experiment.

Reaction of IrI(CO)(dppe) with HBr . 0.2 mL (5 equiv) of HBr (99.85%) was added via syringe to a C_6D_6 solution containing 1 mg of IrI(CO)(dppe) in a septum capped NMR tube and the sample was analyzed by ^1H NMR spectroscopy.

Preparation of $\text{IrHBr}_2\text{(CO)(dppe)}$. 1 mL (0.011 mmol) of 47% HBr was added to 1 mL of an orange benzene solution containing 51 mg (0.073 mmol) of IrBr(CO)(dppe) . The mixture was stirred for 2 hours during which a light yellow precipitate formed and the solution turned nearly colorless. The precipitate was collected by filtration and washed with benzene to give 41 mg (74%) of $\text{IrHBr}_2\text{(CO)(dppe)}$. Recrystallization from $\text{CH}_2\text{Cl}_2/\text{EtOH}$ gave a cream colored precipitate. Anal. Calcd for $\text{IrHBr}_2\text{(CO)(dppe)}$: C, 41.60; H, 3.23; P, 7.94. Found: C, 41.00; H, 3.54; P, 7.94.

resonance at δ -8.48 disappears as the δ -16.64 peak becomes larger and a new hydride resonance at δ -8.34 (dd, $J_{PH} = 8.5, 153.5$ Hz) appears. After 70 minutes an apparent equilibrium has been reached between the δ -16.64 complex (9%) and the δ -8.34 species (7%). Figure 1 shows 1H NMR spectra of the reaction of $IrBr(CO)(dppe)$ with 1.25 equivalents of Et_3SiH . The first spectrum was taken after three minutes of reaction at 8°C and consists mainly of resonances assigned to the kinetic product with the hydride multiplet at δ -8.48 (see Table I for peak assignments). The second spectrum was taken after several hours of reaction at 25°C and contains predominantly the thermodynamic product with the hydride resonance at δ -16.64.

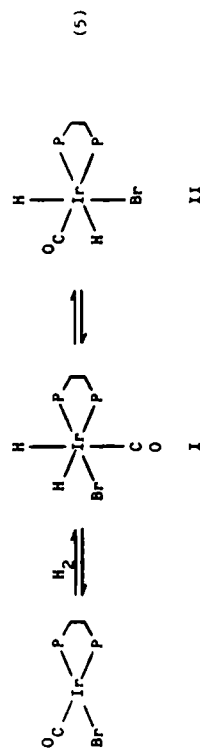
Similar results are obtained when the reaction is carried out in acetone solution. After three minutes two hydride resonances are observed at δ -8.73 (-t, $J_{PH} = 17.9$ Hz) and δ -16.96 (dd, $J_{PH} = 5.9, 15.3$ Hz) in the relative amounts 76% and 24%, respectively, while a third hydride species appears over the course of an hour at δ -8.86 (dd, $J_{PH} = 8.5, 151$ Hz) as the mixture reaches an equilibrium. After 54 hours, the composition of hydride species in the acetone solution corresponds to 3.5% of the δ -8.73 compound, 88% of the δ -16.96 compound, and 8.5% of the δ -8.86 species. The three hydride resonances at δ -8.73, -16.96, and -8.86 in acetone and at δ -8.48, -16.64, and -8.34 in benzene are assigned to 1a, 2a, and 3a, respectively, in eqn (4).



The stereoselectivity of Et_3SiH addition to $IrBr(CO)(dppe)$ has also been examined at -33°C in acetone solution by ^{31}P NMR spectroscopy. Initially, only

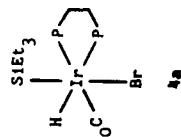
resonances assigned to 1a are observed at δ 35.9 and 16.8, indicating that the amount of 2a present must be $\leq 1\%$. Upon warming, new resonances appear at δ 27.3 and 24.3 for isomer 2a. Selective 1H decoupling experiments confirm that none of the observed resonances assigned to 1a and 2a are coupled to a trans hydride ligand.

The rapid formation of 1a and slower formation of 2a parallels exactly the chemistry seen in the oxidative addition of H_2 to $IrX(CO)(dppe)^1$, shown in eqn (5) for $X = Cl, Br$, and I . For both Et_3SiH and H_2 , oxidative addition proceeds under kinetic control along the $P-Ir-CO$ axis of $IrX(CO)(dppe)$ (pathway I in eqns (1) and (3)), and then isomerization occurs forming the thermodynamically preferred isomer (2a or II) which corresponds to oxidative addition along the $P-Ir-X$ axis (pathway II). An additional stereochemical feature of the Et_3SiH reaction is that although two substrate orientations are possible for each pathway of addition, the reaction kinetically favors the isomers that have mutually trans silyl and phosphine ligands, i.e., the HC product in pathway I (1a) and the HX product in pathway II (2a). The hydride resonances in 1a and 2a agree closely in chemical shift and J_{PH} coupling constants with the corresponding hydride resonances in I and II of eqn (5) (see Table I).



The assignment of structure 3a for the third product, which exhibits a hydride resonance at δ -8.34 in benzene and -8.86 in acetone and remains a minor isomer, is based on the magnitude of $J_{PH}(trans)$. Examination of Table I shows

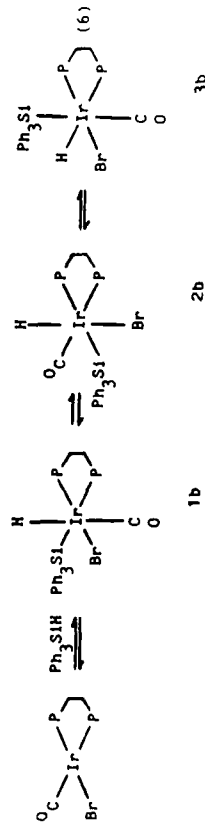
that the observed J_{PH} of 151 Hz (acetone) and 153.5 Hz (benzene) agrees more closely with *trans* J_{PH} of 152.2 Hz seen in I than with the corresponding value of 132.9 Hz in II. Structure 3a arises from the oxidative addition of Et_3SiH along the kinetically preferred direction of addition, pathway I, but with the HP substrate orientation. The alternative assignment for this product is structure 4a which would result from oxidative addition in the less favorable direction, pathway II, with the HP substrate orientation. We think this is a less likely possibility. While the assignment of 3a to the third product



formed in the reaction between Et_3SiH and $IrBr(CO)(dppe)$ is not unambiguous, the assignment does not affect analysis of the kinetic diastereoselectivity of the reaction leading to 1a over the thermodynamically most stable isomer 2a.

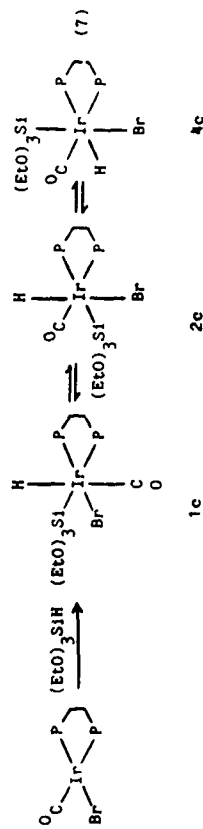
Reaction of Ph_3SiH , $(EtO)_3SiH$, Me_2ClSiH , and $MeCl_2SiH$ with $IrBr(CO)(dppe)$.

The reaction of $IrBr(CO)(dppe)$ with Ph_3SiH also leads to the formation of three isomers of $IrHBr(SiPh_3)(CO)(dppe)$, 1b, 2b, and 3b, eqn (6). Six minutes after



adding benzene to $IrBr(CO)(dppe)$ and three equivalents of Ph_3SiH the 1H NMR spectrum shows two hydride resonances at δ -7.98 (dd, J_{PH} = 16.7, 19.1 Hz) and δ -15.97 (dd, J_{PH} = 6.5, 17.0 Hz) assigned to isomers 1b and 2b, respectively, by analogy to the corresponding triethylsilyl compounds 1a and 2a (see Table I). The relative amounts of 1b and 2b are 91% and 9% in the spectrum at t=6 min. Isomerization to a mixture of three isomers occurs over several hours, eventually reaching an equilibrium of 2% 1b, 93% 2b, and 5% 3b. Complex 3b is characterized by a hydride resonance at δ -7.91 (dd, J_{PH} = 8.0, 151.9 Hz). The isomerization reaction follows first-order kinetics for the disappearance of 1b until approaching equilibrium with k = 0.015 min^{-1} at 23°C.

The reaction of $IrBr(CO)(dppe)$ with $(EtO)_3SiH$ follows a similar pattern where kinetic isomer 1c forms initially and then isomerizes to an equilibrium mixture of three isomers, eqn (7). In this case, unequivocal assignments for the three isomers can be made based on a combination of 1H and ^{13}C NMR experiments. ^{13}C -enriched $IrBr(CO)(dppe)$ (88% ^{13}C) was prepared by stirring a THF solution of $IrBr(CO)(dppe)$ under ^{13}CO at 50°C for 10 minutes and then precipitating the product. In the experiment using unlabelled $IrBr(CO)(dppe)$, the 1H NMR spectrum taken six minutes after the addition of one equivalent of

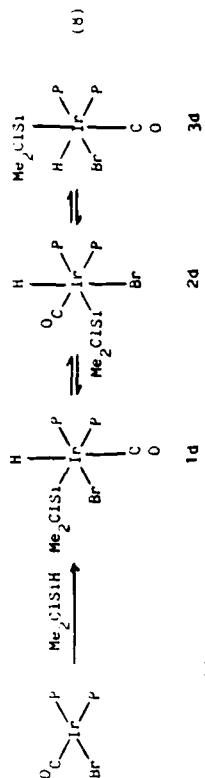


$(EtO)_3SiH$ shows that a single silyl hydride product (2 99%) has formed characterized by a hydride resonance at δ -8.51 (-t, J_{PH} = -18.2 Hz). In the

parallel experiment using ^{13}C -enriched $\text{IrBr}(\text{CO})(\text{dppe})$, the hydride resonance appears at δ 8.50 and contains an additional doublet splitting of 42.8 Hz due to coupling to the trans ^{13}CO ligand as expected for isomer 1c. The ^{13}C NMR spectrum shows a resonance at δ 176.8 (d of -t, $J_{\text{HC}} = 42.8$ Hz, $J_{\text{PC}} = 4.2$ Hz) and ^1H decoupling confirms that the 42.8 Hz coupling is due to the hydride ligand.

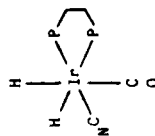
Complex 1c isomerizes much more slowly than the triethylsilyl and triphenylsilyl derivatives with a half-life of 45 hours at room temperature. The thermodynamic product 2c is characterized by a hydride resonance at δ -16.49 (dd, $J_{\text{PH}} = 6.7, 15.4$ Hz). In the ^{13}C -enriched sample, this resonance contains an additional doublet splitting of 4.6 Hz due to the cis ^{13}CO ligand. The ^{13}CO resonance for 2c appears at δ 175.01 (ddd, $J_{\text{HC}} = 4.6$ Hz, $J_{\text{PC}} = 6.7, 118.7$ Hz). The large phosphorus-carbon coupling confirms that the ligands are trans to each other. The third isomer formed must be 4c based on the phosphorus coupling constants of the hydride resonance at δ -8.32 (dd, $J_{\text{PH}} = 17.4, 127.6$ Hz) and the ^{13}C NMR spectrum. The J_{PH} values compare favorably with those for the corresponding hydride in complex II ($J_{\text{PH}} = 17.2, 132.9$ Hz), and differ considerably from the couplings observed for diastereomers 3a ($J_{\text{PH}} = 8.5, 153.5$ Hz) and 3b ($J_{\text{PH}} = 8.0, 151.9$ Hz) from other silane additions. The ^{13}CO resonance for 4c appears at δ 175.17 (ddd, $J_{\text{HC}} = 4.6$ Hz, $J_{\text{PC}} = 6.3, 120$ Hz), and the 120 Hz phosphorus-carbon coupling confirms that the CO ligand is trans to phosphorus. At equilibrium the three diastereomers for $(\text{EtO})_3\text{SiH}$ addition are present in the relative amounts 5% 1c, 76% 2c, and 19% 4c.

The reaction of $\text{IrBr}(\text{CO})(\text{dppe})$ with Me_2ClSiH forms initially the kinetic product 1d which isomerizes upon heating ($t_{1/2} = 20$ min at 72°C) to two other isomers assigned as 2d and 3d, eqn (8). The assignments are based on the ^1H NMR data in Table I and comparison with those for the analogous Et_3Si , Ph_3Si , and $(\text{EtO})_3\text{Si}$ derivatives.

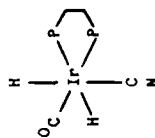


The oxidative addition of MeCl_2SiH to $\text{IrBr}(\text{CO})(\text{dppe})$ yields the usual kinetic product, 1e (see NMR data in Table I), but unlike the other silyl hydride products, no isomerization is observed, even upon heating the sample for one hour at 74°C . It appears that the isomerization rates for 1a-e are influenced by the electronegativity of the substituents on silicon such that the more electronegative substituents Cl and OEt slow the rate of isomerization.

All four of the observed diastereomers of $\text{IrHBr}(\text{SiR}_3)(\text{CO})(\text{dppe})$, 1-4, contain cis hydride and silyl ligands, and can in principle form by cis oxidative addition of R_3SiH to $\text{IrBr}(\text{CO})(\text{dppe})$. If the isomerization of the initially formed diastereomer, 1, proceeds via reductive elimination of R_3SiH , followed by oxidative addition with different stereochemistry, then the rate of R_3SiH reductive elimination from 1 must be fast compared to the rate of isomerization in order to account for the observed diastereoselectivity of R_3SiH oxidative addition favoring isomer 1. To test this hypothesis, we have attempted to measure the rate of reductive elimination of Ph_3SiH from 1b by adding $(\text{EtO})_3\text{SiH}$ to a benzene solution of 1b. A ^1H NMR spectrum taken four minutes after addition of 3.5 equivalents of $(\text{EtO})_3\text{SiH}$ shows only resonances for 1c and the amount of 1b present must be $< 2\%$ at this time. Assuming that the reaction proceeds via initial Ph_3SiH reductive elimination as in eqn (9), this result indicates that the half-life of Ph_3SiH reductive elimination at 23°C is



III



IV

addition (pathway 1) is favored both kinetically and thermodynamically for the two substrates Et₃SiH and H₂.

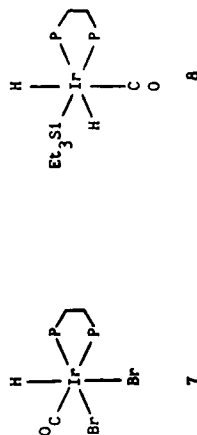
In the later stages of the isomerization reaction of eqn (12), a secondary reaction is observed whereby the IrH(CN)(SiEt₃)(CO)(dppe) stereoisomers 5 and 6 are converted to IrH₂(CN)(CO)(dppe) (three isomers are in equilibrium¹⁴) with concomitant consumption of Et₃SiH and formation of Et₃SiSiEt₃. The ¹H NMR spectrum after 3.5 hours shows new hydride peaks at δ -10.11 and δ -10.86 identical to those of compound III, and the relative amounts of products are 37% 5, 37% 6, and 26% III. After 25 hours there is 16% 5, 8% 6, and 76% isomers of IrH₂(CN)(CO)(dppe). Figure 2 shows ¹H NMR spectra in the triethylsilyl region at different stages of the reaction. Eventually, ~95% of the triethylsilyl functional group is converted to Et₃SiSiEt₃ (δ 0.94 (t, CH₃, J = 7.9 Hz), 0.53 (q, CH₂)), two equivalents of Et₃SiH were used initially, at which time >90% of the iridium containing species occurs as IrH₂(CN)(CO)(dppe).

Examination of the IrBr(CO)(dppe) + Et₃SiH samples, which were also prepared in sealed NMR tubes, reveals that secondary reaction chemistry is also occurring for the IrHBr(SiEt₃)(CO)(dppe) isomers. The sample in acetone that originally contained IrBr(CO)(dppe) and one equivalent of Et₃SiH becomes orange-yellow color while sitting in the dark at room temperature for one year, and the ¹H NMR spectrum shows that the color is due to the regeneration of IrBr(CO)(dppe). The complex IrBr(CO)(dppe) is identified by its four methylene resonances at δ 2.75, 2.68, 2.42, and 2.36 which integrate as 45% of the total dppe methylene peaks.

Three major hydride products are also observed along with two organosilicon products. Integration of the hydride resonances against the phenyl region indicates that 25% of the dppe-containing species corresponds to the dihydride compound II which is partially deuterated (12% corresponds to the H₂ complex and 13% to the HD isotopomers as determined by direct integration of the resolved hydride resonances; a small amount of the D₂ isotopomer may also be present).

The other two hydride components of the dppe-containing species are the monohydride IrHBr₂(CO)(dppe), 7, (δ -15.85 (dd, J_{PH} = 11.2, 15.5 Hz)), present as 8.5% of the dppe-containing species, and the dihydride IrH₂(SiEt₃)(CO)(dppe), 8, (δ -10.73 (dd, J_{PH} = 11.1, 115.7 Hz) and δ -11.09 (t, J_{PH} = 19.3 Hz)) present as 11% of the total. Complex 7 has been independently prepared from

IrBr(CO)(dppe) + HBr as described in the next section. Complex 8 has been independently prepared from IrH₃(CO)(dppe) and Et₃SiH by heating a benzene solution at 73°C for 20 minutes (quantitative yield by ¹H NMR spectroscopy).



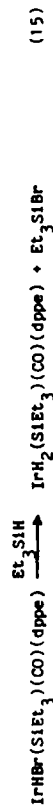
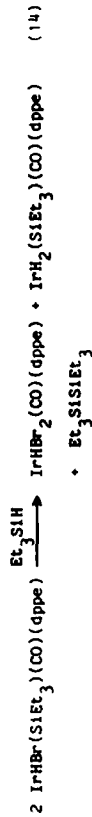
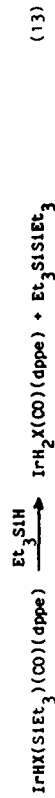
7

8

The triethylgermyl analog of 8, IrH₂(GeEt₃)(CO)(dppe), has been reported²¹ and the ¹H NMR spectra of the two compounds in benzene solution are very similar: δ -10.04 (dd, J_{PH} = 11, 121 Hz), -10.82 (t, J_{PH} = 19 Hz) for the germyl compound, and δ -10.02 (dd, J_{PH} = 11.0, 117.0 Hz), -10.69 (t, J_{PH} = 19.1 Hz) for the silyl compound. The initial organosilicon product is Et₃SiSiEt₃ (δ 0.94 (t, CH₃, J = 8.0 Hz), 0.53 (q, CH₂)) while at longer times peaks apparently due to Et₃SiOSiEt₃ appear (δ 0.94 (t, CH₃, J = 8.0 Hz), 0.57 (q, CH₂)).

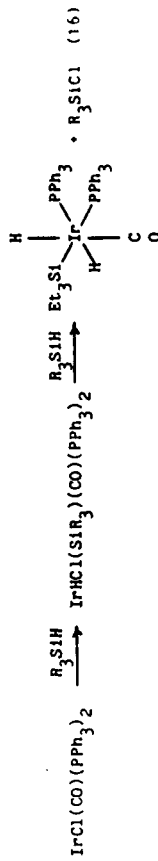
Similar results are obtained for the sample in benzene prepared from $\text{IrBr}(\text{CO})(\text{dppe})$ and three equivalents of Et_3SiH . After 25 days at room temperature the sample contains 75% $\text{IrHBr}(\text{SiEt}_3)_3(\text{CO})(\text{dppe})$ (70.5% 2a and 4.5% 3a), 1% $\text{IrH}_2\text{Br}(\text{CO})(\text{dppe})$ (II), 11% $\text{IrHBr}_2(\text{CO})(\text{dppe})$ (7), and 13% $\text{IrH}_2(\text{SiEt}_3)_3(\text{CO})(\text{dppe})$ (8). Upon further standing a small amount of colorless crystals forms as the hydride resonance for 7 diminishes. The amount of complex 8 continues to increase at the expense of 2a and 3a, and a new organosilicon product is observed, Et_3SiBr (δ 0.89 (t, CH_3 , $J = 7.8$ Hz), 0.67 (q, CH_2); mass spectrum, parent ions observed at m/e 194, 196). After one year at room temperature a small amount of precipitate remains and the relative solution composition of dppe-containing species based on integration of hydride resonances is 16% 2a, 6% II, and 78% 8. From analysis of the triethylsilyl spectral region (based on three equivalents of Et_3SiH) there exists 0.54 equivalent of Et_3SiBr , 0.19 equivalent of $\text{Et}_3\text{SiSiEt}_3$, and 1.23 equivalents of unreacted Et_3SiH (along with 0.72 equivalent of 8 and 0.15 equivalent of 2a).

The secondary chemistry of the reaction systems $\text{IrX}(\text{CO})(\text{dppe}) + \text{Et}_3\text{SiH}$ ($X = \text{CN}, \text{Br}$) follows the stoichiometries of eqns (13) - (15). The observed products



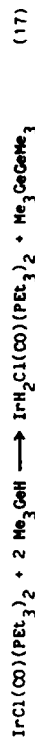
can be accounted for within the framework of $\text{Ir}(\text{III})/\text{Ir}(\text{I})$ reductive elimination/oxidative addition steps by the reactions in Scheme I. Reductive elimination of HX from $\text{IrHX}(\text{SiEt}_3)_3(\text{CO})(\text{dppe})$ and subsequent reactions involving Et_3SiH and HX lead to either the formation of one equivalent each of $\text{IrH}_2\text{X}(\text{CO})(\text{dppe})$ and $\text{Et}_3\text{SiSiEt}_3$ as in eqn (13), or the formation of equimolar amounts of 7, 8, and $\text{Et}_3\text{SiSiEt}_3$ as in eqn

(14). Eqn (15) represents an alternative route to 8 that does not result in $\text{Et}_3\text{SiSiEt}_3$ formation. In eqn (15) the reductive elimination of Et_3SiBr from $\text{IrHBr}(\text{SiEt}_3)_3(\text{CO})(\text{dppe})$ is followed by Et_3SiH oxidative addition to $\text{IrH}(\text{CO})(\text{dppe})$ yielding the silyl dihydride product. There is ample literature precedent for eqn (15) as both Glockling, *et al.*,¹⁰ and Chalk^{6b} have reported analogous chemistry with Vaska's complex, eqn. (16). The initial oxidative addition product, $\text{IrHCl}(\text{SiR}_3)_3(\text{CO})(\text{PPh}_3)_2$, has been isolated for $R = \text{OEt}$ and Cl ,^{6a,8} and is



presumed to form for $R = \text{Me}$ and Et as an unstable intermediate in eqn (16).

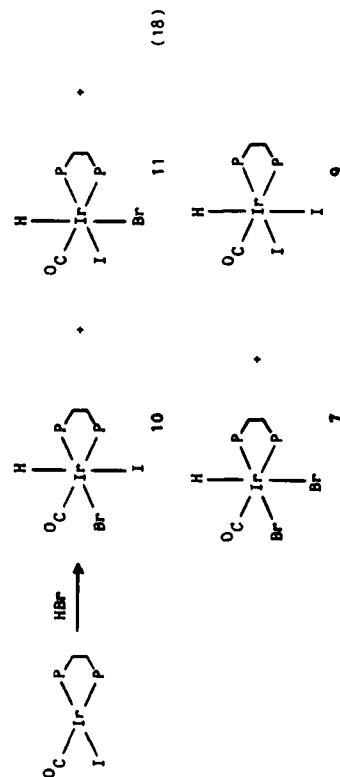
Parish and coworkers^{8c} have also proposed that R_3SiCl reductive elimination occurs from $\text{IrHCl}(\text{SiR}_3)_3(\text{CO})(\text{PPh}_3)_2$ in catalytic H/D exchange reactions of $\text{R}_3\text{SiH}/\text{D}_2$ and $\text{R}_3\text{SiH}/\text{R}_3\text{SiD}$. Vaska's complex reacts with trialkylgermanes in the same manner as eqn (16), giving $\text{IrH}_2(\text{GeR}_3)_2(\text{CO})(\text{PPh}_3)_2$ and R_3GeCl , and, at longer times, H_2 and R_3GeGeR_3 .²¹ When the triethylphosphine derivative of Vaska's complex is used, the reaction is selective for digermane formation, eqn (17), paralleling our results in eqn (13). As shown in Scheme I, we believe that



$\text{Et}_3\text{SiSiEt}_3$ is most likely formed via the intermediate $\text{Ir}(\text{SiEt}_3)_3(\text{CO})(\text{dppe})$ which formally results from HX reductive elimination. It is not clear at this time whether unimolecular HX elimination occurs from $\text{IrHX}(\text{SiEt}_3)_3(\text{CO})(\text{dppe})$, but, in a possibly related reaction, we have observed that the corresponding dihydride complex II undergoes base-promoted dehydrohalogenation forming the intermediate

$\text{IrH}(\text{CO})(\text{dppe})$.¹ Also noteworthy with regard to the intermediacy of $\text{Ir}(\text{SiEt}_3)(\text{CO})(\text{dppe})$ and $\text{IrH}(\text{SiEt}_3)_2(\text{CO})(\text{dppe})$ in Scheme I is the isolation of the germyl $\text{Ir}(\text{I})$ compounds $\text{Ir}(\text{C}_6\text{H}_5)_3(\text{CO})(\text{PPh}_3)_2$ ($R = \text{Me}, \text{Et}$),²¹ and the chelated dialkyl hydride compound $\text{IrH}(\text{SiMe}_2\text{OSiMe}_2)_2(\text{CO})(\text{PPh}_3)_2$ (prepared from Vaska's complex and $\text{HMe}_2\text{SiOSiMe}_2\text{H}$).¹² Thus, reasonable precedents exist for all of the intermediates proposed in Scheme I.

Reaction of $\text{IrX}(\text{CO})(\text{dppe})$ with HY ($X = \text{Br}, \text{I}; Y = \text{Br}, \text{I}$). To an orange solution of $\text{IrI}(\text{CO})(\text{dppe})$ in C_6D_6 was added 5 equivalents of gaseous HBr giving a colorless solution which was analyzed by ^1H NMR spectroscopy. The ^1H NMR spectrum shows complete conversion to one major monohydride product which slowly interconverts with three other monohydride species (see Figure 3). Two of the later products are identified as $\text{IrHBr}_2(\text{CO})(\text{dppe})$, **7** ($\delta -15.38$ (dd, $J_{\text{PH}} = 10.6, 15.6$ Hz)), and $\text{IrHI}_2(\text{CO})(\text{dppe})$, **9** ($\delta -14.02$ (dd, $J_{\text{PH}} = 8.7, 15.7$ Hz)), by independent syntheses from $\text{IrX}(\text{CO})(\text{dppe})$ and HX . The other two products are characterized as isomers of $\text{IrHBrI}(\text{CO})(\text{dppe})$, **10** and **11** in eqn (18), by the chemical shift and splitting pattern of the hydride resonances. Complex **10** has a hydride resonance at $\delta -13.39$ (dd, $J_{\text{PH}} = 10.2, 15.9$ Hz)



indicative of a hydride trans to iodide, while **11** has a hydride resonance at $\delta -15.99$ (dd, $J_{\text{PH}} = 9.1, 15.5$ Hz) indicative of a hydride trans to bromide. The similarity of the cis phosphorus-hydride coupling constants in the four hydride products is in accord with the common $\text{IrHX}_2(\text{CO})(\text{dppe})$ formulation where hydride is trans to X .

Complex **10** is the major initial product in reaction (18), comprising 86% of the mixture, and the other three products slowly increase in abundance over time as shown in Table II. After 550 hours the halide ligands in the four products are nearly randomly distributed (i.e., 25% of each product).

It is clear that of the two isomers of $\text{IrHBrI}(\text{CO})(\text{dppe})$ observed in reaction (18), isomer **10** with cis H and Br ligands is formed preferentially relative to **11** which has trans H and Br ligands. Actually, there are six possible isomers for $\text{IrHBrI}(\text{CO})(\text{dppe})$, and based on the above experiment, one cannot rule out the possibility that **10** is a secondary product from the reaction of $\text{IrI}(\text{CO})(\text{dppe})$ and HBr , and forms by isomerization of a different unobserved isomer.

To investigate this possibility we studied the reaction of $\text{IrBr}(\text{CO})(\text{dppe})$ with HI . The same four products are observed, but now isomer **11** is the major product (70% of the product mixture according to the ^1H NMR spectrum taken after 15 minutes, and only a small amount (~7%) of **10** is observed. The relative amounts of **7** and **9** are 10% and 13%, respectively. Thus the stereochemistry of the halides is reversed for the reaction of $\text{IrBr}(\text{CO})(\text{dppe}) + \text{HI}$ compared to the reaction of $\text{IrI}(\text{CO})(\text{dppe}) + \text{HBr}$, a strong indication that the major product in each reaction is indeed the kinetic product.

The major product in each case of HY addition is the isomer that would be formed by a concerted cis addition of HY along the $P\text{-Ir-X}$ axis in $\text{IrX}(\text{CO})(\text{dppe})$, corresponding to pathway **11** in eqn (3) with HX substrate orientation. This diastereoselection is opposite to that observed for both R_3SiH and H_2 , which add along the $P\text{-Ir-CO}$ axis, pathway **1**, and suggests that the initial interaction of

$\text{IrX}(\text{CO})(\text{dppe})$ with HY ($\text{Y} = \text{halide}$) differs significantly from that with R_3SiH or H_2 .

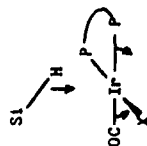
Mechanism of R_3SiH and HY Oxidative Addition and Basis for Stereoselectivity.

The oxidative addition of R_3SiH to $\text{IrX}(\text{CO})(\text{dppe})$ occurs by *cis* addition with kinetically controlled stereochemistry. The initially formed isomer in all cases corresponds to addition along pathway I with *HC* preferred substrate orientation. For $\text{IrBr}(\text{CO})(\text{dppe})$, rapid formation of the *i-HC* kinetic isomer is followed by slower formation of the isomer corresponding to pathway II addition with *HX* orientation. This latter isomer is the most stable of the four possible diastereomers of *cis* silane addition to $\text{IrBr}(\text{CO})(\text{dppe})$. In the case of $\text{Ir}(\text{CN})(\text{CO})(\text{dppe})$, the same diastereoselectivity of silane addition is observed (>99.5% *i-HC* initially) but the relative stability of the diastereomers changes such that the kinetic isomer is also the most stable isomer.

With regard to both the kinetic diastereoselectivity and relative stability of product isomers, the oxidative addition of R_3SiH to $\text{IrX}(\text{CO})(\text{dppe})$ shows remarkable parallels to that reported previously for H_2 ,¹ strongly suggesting the same mechanism of addition for R_3SiH and H_2 . In the prior analysis of H_2 stereoselectivity, we discussed the preference for addition via pathway I over II in terms of H_2 approach to the metal complex in a concerted process, and suggested two factors which would work to favor A (H_2 parallel to P-Ir-CO) over B (H_2 parallel to P-Ir-X). These factors are: (1) an orbital overlap effect wherein the π^* orbital of CO enhances the back-bonding interaction between a filled metal d_{xy} orbital and $\pi^*(\text{H}_2)$ through increased overlap; and (2) a preferred bending of the set of trans ligands P and CO which become *cis* to each other and trans to the hydride ligands in the product. The latter factor is based on the notion that H_2 addition to the metal complex is similar to forming an adduct with an electron pair donor. As the H_2 substrate approaches the metal

complex in this addition, one pair of trans ligands bends such that complex + substrate form a trigonal bipyramid as the transition state. The bending ligands and the H_2 substrate occupy the equatorial sites of this trigonal bipyramid. Preference for bending of the P-Ir-CO axis over the P-Ir-X axis occurs because this places the better π -acid ligand CO in the equatorial plane where it can better stabilize the developing trigonal bipyramid. This view is similar to that used to explain the trans effect in square planar substitution reactions,²² and relates to the proposal put forth by Harrod³ and shown as C that deformation of the square planar complex is a major component of the activation barrier in H_2 oxidative addition. Both of the factors proposed to explain H_2 stereoselectivity can be extended to silane oxidative addition as well.

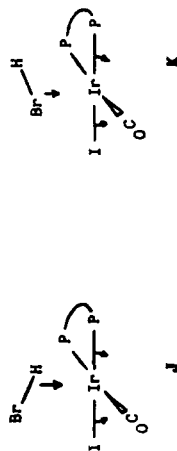
The question of relative substrate orientation does not arise in the oxidative addition chemistry of H_2 but must be addressed for silanes. For addition of Si-H along P-Ir-CO , pathway I, the formation of the *HC* isomer as the kinetic isomer corresponds to a clear preference of Si-H approach shown in D to that shown in E. The basis of this preference is probably steric and involves minimizing non-bonded interactions between the silyl group and the phosphine substituents. Approach D makes the silyl group *cis* to only one of the phosphines and trans to the other. Similarly for addition along pathway II, approach F is favored over G, leading to formation of the *HX* isomer with R_3Si *cis* to one P donor and trans to the other. Steric interactions may also alter silane approach to the metal complex such that the Si-H bond is not parallel to the P-Ir-CO axis but rather is tilted towards an "end-on" approach, H, which emphasizes the hydridic character and donor ability of the Si-H bond. Thus, the relative importance of bending the P-Ir-CO axis to stabilize the developing trigonal bipyramid increases in H relative to D, while that of the overlap



M

effect involving $\pi^*(\text{CO})$ and the back-bonding interaction between filled metal d and $\sigma^*(\text{Si-H})$ is significantly diminished. If the more end-on approach depicted in M does in fact occur for Si-H oxidative addition, then the observed stereochemical similarities of silane and H_2 addition suggest that the second factor given above (i.e., the relative ease of bending trans ligands) is the more important factor in determining the observed diastereoselectivity for both substrates.

The observation that hydrogen halides oxidatively add to $\text{IrX}(\text{CO})(\text{dppe})$ in the opposite direction, along the P-Ir-X axis, pathway 11, clearly indicates that the ease of trans ligand deformation or bending in $\text{IrX}(\text{CO})(\text{dppe})$ without regard to incoming substrate cannot by itself account for the stereoselectivity of these oxidative addition reactions. Thus, the complex-substrate interaction must be substantially different for HX vs. H_2 and R_3SiH . The first question that must be addressed is whether the HX addition is concerted or proceeds in two or more discrete steps. The stereoselective nature of the reaction where H and X ligands occupy cis positions in the kinetic product strongly suggests a concerted mechanism. In such a mechanism, the approach of the highly polar species HX along the P-Ir-I axis of $\text{Ir}(\text{CO})(\text{dppe})$ will undoubtedly be unsymmetrical, and can be either electrophilic or nucleophilic in character as shown in J and K, respectively. If HBr approach is nucleophilic as in K the



J

situation resembles that of silane approach M and similar considerations would apply regarding the diastereoselectivity. Thus, the developing trigonal bipyramid of $\text{Ir}(\text{CO})(\text{dppe}) + \text{HBr}$ would be more stable with the better π -acid CO in the equatorial plane than with iodide there, and the concerted addition of HBr would be expected to proceed along P-Ir-CO, pathway 1. This expectation is contrary to what is observed.

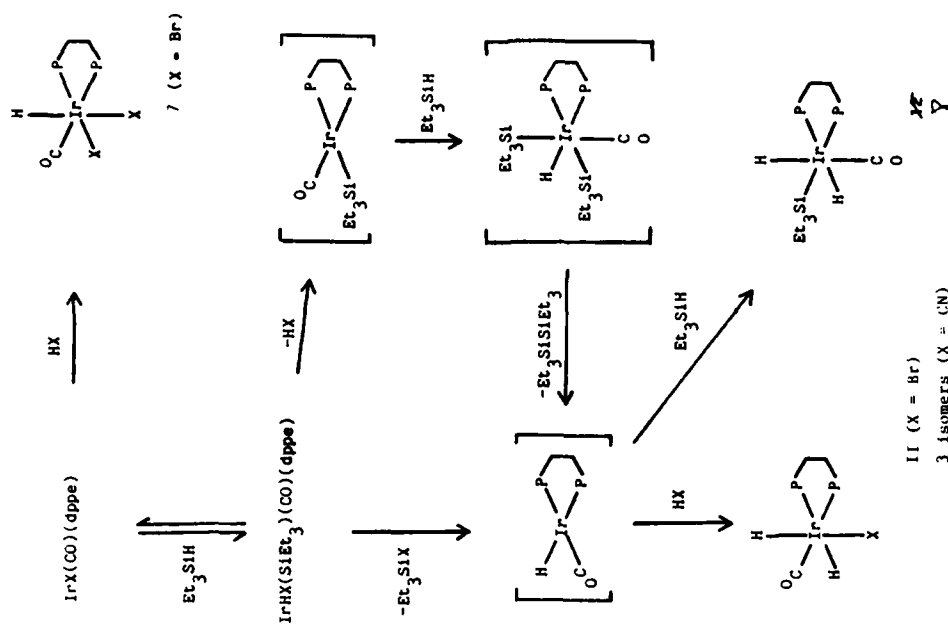
For electrophilic approach J, the bending of P-Ir-I leads to a complex + substrate trigonal bipyramid having the better donor iodide in the equatorial plane thus enhancing the ability of Ir(I) to donate electrons to an incoming electrophile. It is well established that $\text{Ir}(\text{I})$ complexes can act as electron pair donors as in the reactions of $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ with BF_3 and MO^+ , and the oxidative addition reaction of MeI. In the present case, the donor ability of the Ir complex is better if P-Ir-X bends than if P-Ir-CO bends, and this leads to the observed diastereoselectivity. The primary interaction of hydrogen halides with $\text{IrX}(\text{CO})(\text{dppe})$ in nonpolar media, while leading to concerted addition, clearly differs from that of H_2 and R_3SiH . We conclude that in concerted oxidative addition reactions to cis phosphine analogs of Vaska's complex, the stereochemistry of addition (i.e., pathway 1 or 11) can be controlled kinetically by the nucleophilic or electrophilic character of the substrate.

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Scheme 1



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20. A small amount (4%) of a second hydride product characterized as $\text{IrH(CN)}_2\text{(SiEt}_3\text{)(dppe)}^-$ with H trans to CN (δ -13.74 (dd, $J_{\text{PH}} = 12.3, 16.5$ Hz)) was also observed. This complex was independently prepared from $\text{Ir(CN)}_2\text{(CO)(dppe)}^-$ and Et_3SiH , indicating that its formation above was due to the use of a slight excess of PPH(CN) relative to IrBr(CO)(dppe) .
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Table I. ¹H NMR Data of Hydride Complexes.^a

Compound	$\delta_{\text{IrH}}(^1\text{PPh})$	$\delta_{\text{CH}_2}(\text{dppe})$	$\delta_{\text{O-Ph}}(\text{dppe})$	$\delta(\text{R}_2\text{Si})$	IrHBr(SiMe ₃) ₃ (CO)(dppe), 1d	
IrHBr(SiEt ₃) ₃ (CO)(dppe), 1a	-8.48(-17.8)	2.02(1H) ^b 1.83(2H) ^b 1.49(1H) ^b	8.02(2H) 7.77(2H) 7.53(4H)	1.39(3H) ^b [82.981] ^b 1.15(3H) ^b	-8.60(-18.3)	2.23(1H) 1.76(3H) 7.96(2H) 7.70(4H) 7.62(2H) 1.53(3H) 1.43(3H)
2a	-16.64(5.8, 15.1)	3.02(1H) 2.20(2H) -1.22(1H) ^c	7.85(2H) 7.57(4H) 7.46(2H)	1.21(15H)	2d -16.03(7.3, 14.1)	2.99(1H) 2.30(1H) 2.20(1H) 1.12(1H) 7.80(4H) 7.51(2H) 7.31(2H) 1.25(3H) 0.54(3H)
3a	-8.34(8.5, 153.5)				3d -8.60(9.5, 150.2)	
IrHBr(SiPh ₃) ₃ (CO)(dppe), 1b	-7.98(16.7, 19.1)	2.12(1H) 1.83(1H) 1.65(2H)	8.04(2H) 7.73(2H) 7.32(2H)	7.94(6H, o-Ph)	1e -8.77(-16.8)	2.14(1H) 1.86(1H) 1.67(2H) 7.91(2H) 7.60-7.70(6H) 1.84(3H)
2b	-15.97(6.5, 17.0)	2.77(1H) 2.17(1H) 1.77(1H) 1.60(1H)	7.54(2H) 7.47(2H) 7.26(2H)	7.96(6H, o-Ph)	5 ^d -10.05(-17.3)	2.60(2H) 2.25(1H) 7.96(4H) 0.86(9H) 0.78(3H) 0.62(3H)
3b	-7.91(8.0, 151.9)				6 ^d -10.13(8.9, 124)	0.86(9H)
IrHBr(Si(OEt) ₃) ₃ (CO)(dppe), 1c	-8.51(-18.2)	2.15(1H) 1.68-1.88(3H)	8.02(2H) 7.86(2H) 7.77(2H) 7.64(2H)	4.31(3H) 4.17(3H) 1.25(9H)	7 -15.85(11.2, 15.5)	3.24(1H) ^e 2.98(1H) ^e 2.53(1H) ^e 2.13(1H) ^e 7.83(2H) ^e 7.73(2H) ^e 7.60(2H) ^e 7.53(2H) ^e
2c	-16.49(6.7, 15.4)	2.77(1H) 2.37(1H) 2.00(1H) 1.50(1H)	8.01(2H) 7.77(2H) 7.56(2H) 7.40(2H)	4.07(3H) 3.99(3H) 1.20(9H)	8 -10.73(11.1, 115.7) -11.09(19.3)	2.18(1H) 1.99(2H) 1.78(1H) 7.90(2H) 7.63(2H) 7.52(2H) 7.46(2H) 1.31(4H) 1.11(6H)
4c	-8.32(17.4, 127.6)				9 -14.02(8.7, 15.7)	

Table I, continued

$\text{IrHBr}(\text{CO})(\text{dppe})$,	10	-13.39(10.2,15.9)	2.8(1H)	7.93(2H)
			2.39(1H)	7.85(2H)
			1.91(1H)	7.34(2H)
				7.27(2H)
	11	-15.99(9.1,15.5)		
$\text{IrH}_2\text{Br}(\text{CO})(\text{dppe})$,	I	-7.87(14.2,152.2)	2.29(1H)	8.09(2H)
		-8.94(-19.3)	2.10(1H)	7.97(2H)
			2.03(1H)	7.79(2H)
			1.73(1H)	7.27(2H)
	II	-8.34(17.2,132.9)	2.60(2H)	7.82(2H)
		-17.48(8.6,16.6)	1.92(2H)	7.66(2H)
				7.56(2H)
				7.47(2H)
$\text{IrH}_2(\text{CN})(\text{CO})(\text{dppe})$,	III ^d	-10.13(13.2,129.9)	3.25(1H)	7.97(4H)
		-10.87(-17.9)	2.88(2H)	7.88(2H)
			2.50(1H)	7.67(2H)
	IV ^d	-10.43(16.1,121)		
		-13.27(12.5,19.3)		

Table I Footnotes

^a Spectra are taken from benzene solutions at 400 MHz unless otherwise indicated.

^b Spectrum taken at 6°C.

^c Resonance located by homonuclear decoupling experiments.

^d Acetone solution.

^e CCl_3 solution.

Table II. Percent Composition of the Products from the Reaction of $\text{Ir}(\text{CO})(\text{dppe})$ and HBr .

Time,	$\text{IrHBr}(\text{CO})(\text{dppe})$	$\text{IrHBr}(\text{CO})(\text{dppe})$	$\text{IrHBr}_2(\text{CO})(\text{dppe})$	$\text{IrH}_2(\text{CO})(\text{dppe})$
h	10	11	7	9
0.1	86	4	6	4
14	73	11	11	5
41	66	11	15	8
190	44	17	22	17
550	31	22	25	21

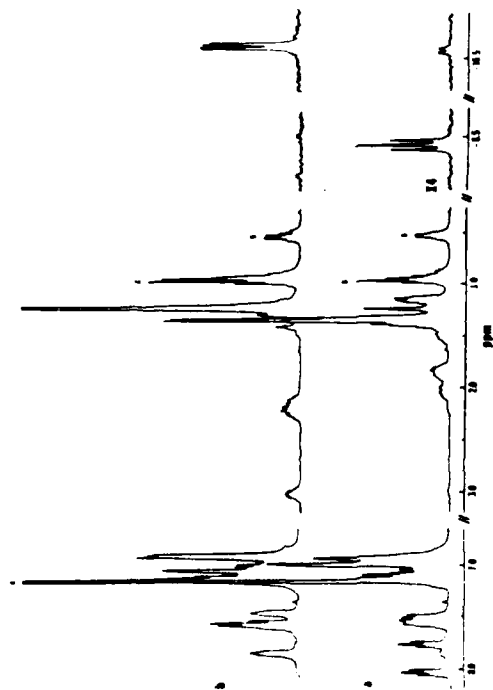


Figure 1. ^1H NMR spectra of the reaction of $\text{IrBr}(\text{CO})(\text{dppe})$ with Et_3SiH (a) after three minutes of reaction at 8°C ; (b) after several hours of reaction at 25°C . The peaks marked "a" are due to excess Et_3SiH , and the peak marked "x" corresponds to benzene solvent ($\text{C}_6\text{D}_5\text{H}$, δ 7.15).

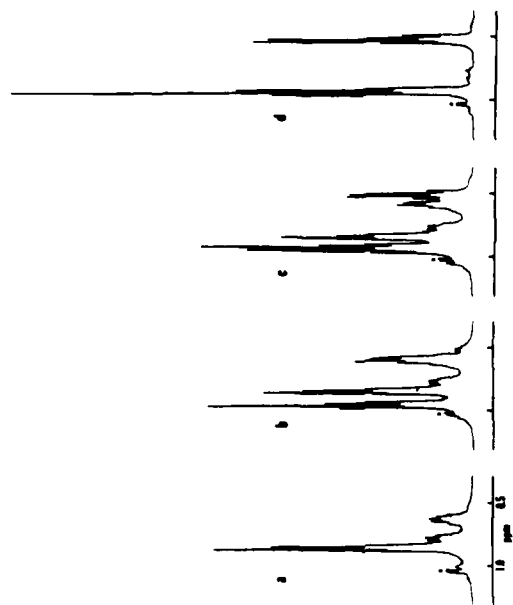


Figure 2. ^1H NMR spectra in the triethylsilyl region for the reaction of $\text{Ir}(\text{CN})(\text{CO})(\text{dppe})$ and Et_3SiH in acetone solution: (a) $\text{Ir}(\text{CN})(\text{CO})(\text{dppe}) + 1.0 \text{ Et}_3\text{SiH}$ after 5 minutes of reaction; (b) $\text{Ir}(\text{CN})(\text{CO})(\text{dppe}) + 2.0 \text{ Et}_3\text{SiH}$ after 12 minutes of reaction; (c) same sample at 207 minutes; (d) same sample after four months. The doublet marked "x" is due to a solvent impurity.

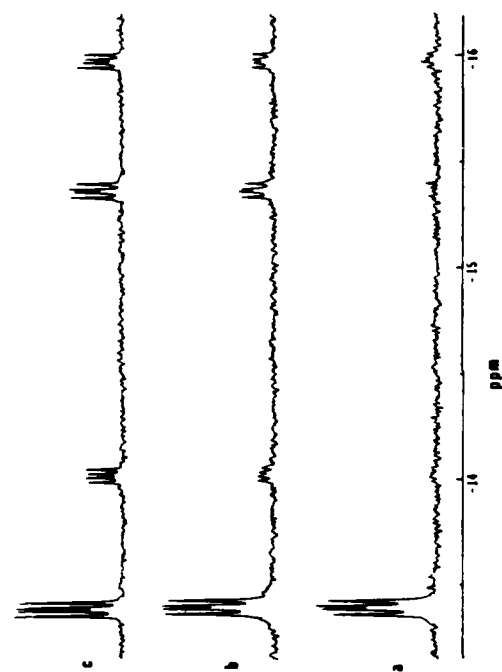


Figure 3. ^1H NMR spectra in the hydride region for the reaction of $\text{IrI}(\text{CO})(\text{dppe})$ with $\text{HBr}(\text{g})$: (a) after 38 minutes of reaction at 25°C ; (b) 41 hours; (c) 190 hours.

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